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Separation of benzene from heptane using tree ionic liquids: $BMimMSO_4$, $BMimNTf_2$, and $PMimNTf_2$

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Abstract

To study the influence of the structure of the different ionic liquids on the separation of the binary mixtures of hydrocarbon + aromatic compounds, we have carried out the liquid-liquid equilibrium (LLE) of the ternary systems: heptane + benzene + 1-butyl-3-methylimidazolium methylsulfate, $BMimMSO_4$, 1-butyl-3-methylimidazolium bistrifluoromethylsulfonylimide, $BMimNTF_2$ and 1-methyl-3-propylimidazolium bistrifluoromethylsulfonylimide, $PMimNTF_2$, were measured at T = 298.15 K and atmospheric pressure. Selectivity and solute distribution ratio, derived from the equilibrium data, were used to determine if these ionic liquid can be used as a potential extracting solvent for the separation of aromatic compounds from heptane. The experimental data for the ternary systems were well correlated with NRTL and UNIQUAC equations. The results were used to analyse the influence of structure of the ionic liquid.

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Keywords: ELL; benzene; heptane; ionic liquids

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1. Introduction

The separation of aromatic hydrocarbons (e.g. benzene, toluene and ethylbenzene) from aliphatic compounds is of great importance for the petrochemical industry for two basic reasons: the first is to meet the high demand of aromatic compounds by chemical industry, and the second reason is the strict legal restrictions on the content of aromatics in gasoline. The aromatic hydrocarbons are separated from naphtha using a typical liquid-liquid extraction process [1]. Some conventional organic chemicals, such as sulfolane, [2-5] N- formyl morpholine, [6] N-methylimidazole, or N-ethylimidazole, [7] glycols, [8-10] propylene carbonate, [11] or combinations of solvents are used for the extraction of aromatics. In separations, a distillation step is usually also necessary to separate the solvent used from extract and raffinate phases. Nevertheless, when the ionic liquids are used the process is much simpler because no distillation step is necessary and the recovery of the ionic liquid solvent is much easier [12].

Among the multiple possible ionic liquids, the most commonly used cations for many applications are those belonging to the 1-alkyl-3-methylimidazolium family, due to the great number of different mixtures and the enormous amount of possible ionic liquids, we will study the influence of the structure of two anions and the length of the cation of the ionic liquids.

This work is a study on the extraction of benzene from heptane using the following ionic liquids: $BMimMSO_4$, $BMimNTf_2$, and $PMimNTf_2$. The liquid-liquid equilibria (LLE) for the ternary systems heptane (1) + benzene (2) + 1-butyl-3-methylimidazolium methylsulfate, $BMimMSO_4$ or 1-butyl-3-methylimidazolium bistrifluoromethylsulfonylimide, $BMimNTF_2$ or 1-methyl-3-propylimidazolium bistrifluoromethylsulfonylimide, $PMimNTF_2$ (3), were determined at T = 298.15 K and atmospheric pressure. From experimental data, it was possible to calculate the selectivity and solute distribution ratio which are widely used parameters to characterize the suitability of a solvent in liquid extraction. These data were also correlated using the NRTL [13] and UNIQUAC [14] equations.

2. Experimental

2.1. Chemicals

Heptane and benzene were supplied by Sigma-Aldrich with purity higher than 99.9 %, in mass fraction. They were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich and kept in an inert argon atmosphere.

The ionic liquid $BMimMSO_4$ used in this work was synthesized in laboratory using standard procedures for other sulfate ionic liquids [15] and the ionic liquids: $BMimNTF_2$ and $PMimNTF_2$ were delivered by IoLiTec. The ionic liquids were kept in bottles with inert gas. Before using, the sample was subjected to vacuum (p = 0.2 Pa) and moderate temperature (T = 323.15 K) for several days to remove possible traces of other solvents and moisture. The water content was determined using a 787 Karl Fischer Titrino and ionic liquids showed that mass fraction of water was less than 7×10^{-4} for each IL

2.2 Apparatus and procedure

LLE data for the studied systems were determined at T = 298.15 K. Solubility curves were obtained by the cloud point method [16], while the tie-line compositions were determined by density measurements.

The density of the pure liquids and mixtures were measured using an Anton Paar DSA-5000 digital vibrating tube densimeter with an uncertainty of $\pm 3\times10^{-5}$ g·cm^{-3}.

The solubility curves of the studied systems were determined at T = 298.15 K and atmospheric pressure by titrating binary mixtures of known compositions with the third component until the transition was visually determined. For the preparation of samples, a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3\times10^{-4}$ g was used. The density of each sample was measured and a polynomial expression for the density as function of composition was. To estimate the error of the technique used for the determination of the solubility curves, three validation points were evaluated. These points were obtained by weighing, and then their densities were determined. The compositions of these points were calculated through the above mentioned polynomial expressions and the obtained values were compared with the experimental compositions. The maximum error was estimated to be ±0.006 in mole fraction.

For the tie-line determination, mixtures with compositions inside the immiscible region were introduced into glass cells and closed using silicon covers. Special care was taken in covering the whole immiscibility region. The temperature was maintained constant in a thermostatic bath (PoliScience digital temperature controller) with a precision of ±0.01 K. To guarantee the thermodynamic equilibrium, the mixtures were agitated using a magnetic stirrer for 6 hrs. in order to allow an intimate contact between phases, and then the equilibrium phases were left overnight at the studied temperature to settle down. Then, a sample from each phase was withdrawn using a syringe to carry out the compositional analysis. The determination of the tie-line compositions for the ternary systems was carried out by correlating the densities of the two immiscible liquid phases of the conjugate solutions with the polynomial expressions of density versus composition. Note that since no ionic liquid was detected in the alkane-rich phase, the composition of this phase was determined using the density data versus molar fraction for the binary systems alkane (1) + aromatic (2). The tie-line compositions are summarized in Table 1.

3. Results and discussion

The experimental LLE data for the ternary systems are reported in Table 1, and the corresponding plots are shown in Figure 2.

Together with the LLE experimental data, Table 1 includes the corresponding values for the solute distribution ratio, β, and the selectivity, S defined bellow:

$$\beta = \frac{x_2^{II}}{x_2^{I}} \tag{1}$$

$$S = \frac{x_2^{II} x_1^{I}}{x_2^{I} x_1^{II}} \tag{2}$$

where x_2^I and x_1^I are the mole fractions of heptane and benzene, respectively, in the upper phase (alkane-rich phase); and x_1^{II} and x_2^{II} are the mole fractions of heptane and benzene, respectively, in the lower phase (IL-rich phase).

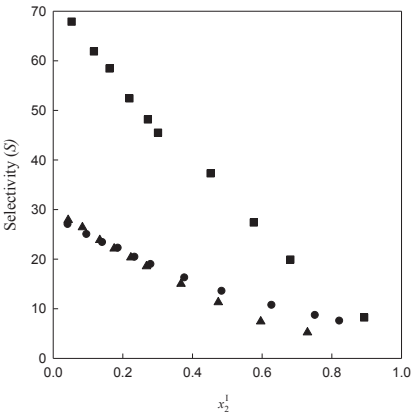
Table 1. Experimental liquid-liquid equilibrium data in mole fraction for ternary systems of heptane (1) + benzene (2) + $BMimMSO_4$, $BMimNTF_2$ and $PMimNTf_2$ (3) at $T = 298.15$ K, and calculated solute distribution ratio, β, and selectivity, S, values

Alkane-rich phase		Ionic liquid-rich phase		β	S
x_1^I	x_2^I	x_1^{II}	x_2^{II}		
heptane (1) + benzene (2) + BMimMSO4 (3)					
0.947	0.053	0.010	0.038	0.72	67.90
0.883	0.117	0.010	0.082	0.70	61.89
0.838	0.162	0.010	0.113	0.70	58.45
0.781	0.219	0.010	0.147	0.67	52.45
0.728	0.272	0.010	0.180	0.66	48.18
0.699	0.301	0.010	0.196	0.65	45.52
0.548	0.452	0.009	0.277	0.61	37.31
0.424	0.576	0.009	0.335	0.58	27.40
0.319	0.681	0.009	0.383	0.56	19.93
0.107	0.893	0.007	0.482	0.54	8.25
heptane (1) + benzene (2) + BMimNTF2 (3)					
0.957	0.043	0.059	0.074	1.72	27.91
0.916	0.084	0.059	0.143	1.70	26.43
0.866	0.134	0.058	0.214	1.60	23.85
0.825	0.175	0.056	0.263	1.50	22.14
0.777	0.223	0.055	0.321	1.44	20.34
0.732	0.268	0.054	0.367	1.37	18.56
0.633	0.367	0.052	0.453	1.23	15.03
0.526	0.474	0.052	0.530	1.12	11.31
0.404	0.596	0.054	0.592	0.99	7.43
0.270	0.730	0.047	0.665	0.91	5.23
heptane (1) + benzene (2) + PMimNTF2 (3)					
0.957	0.043	0.052	0.063	1.47	26.96
0.903	0.097	0.050	0.134	1.38	24.95
0.858	0.142	0.050	0.193	1.36	23.32
0.813	0.187	0.049	0.250	1.34	22.18
0.765	0.235	0.048	0.300	1.28	20.35
0.719	0.281	0.047	0.347	1.23	18.89
0.622	0.378	0.044	0.433	1.15	16.19
0.515	0.485	0.040	0.508	1.05	13.49
0.372	0.628	0.033	0.594	0.95	10.66
0.247	0.753	0.025	0.658	0.87	8.63
0.177	0.823	0.020	0.695	0.84	7.47

The variations of β and S with the composition of the benzene in the raffinate phase are plotted in Figure 1. In this figure an analysis of the influence of the anion and the alkyl chain of the cation of the imidazolium-based ionic liquids on the extraction was evaluated in terms of the solute distribution ration and selectivity. Regarding the influence of the anion, comparing the behavior of the three systems, it can be observed that the S values are higher for the system containing $BMimMSO_4$, and on the other hand, the β values are higher where $BMimNTf_2$ is used as solvent, being higher than the unity at lower compositions of benzene in the upper phase.

The influence of the alkyl chain of the cation of the IL is lower than the influence of the anion on the phase equilibrium; from Figure 1a can be concluded that selectivity values of the systems containing imidazolium-based ILs with NTf_2^- anion are similar, while in Figure 1b it can be observed that β values slightly increase in the order $BMimMSO_4 > PMimMSO_4$

a)



b)

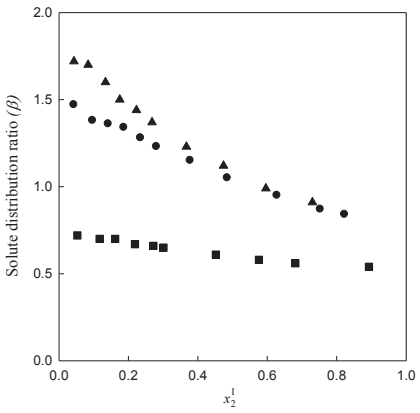


Fig. 1. a) Selectivity, and b) solute distribution ratio for the ternary systems heptane + benzene + ILs as a function of the mole fraction of aromatic compound in the aliphatic-rich phase at T = 298.15 K. Symbols: ■, BMimMSO4; ▲, BMimNTf2; ●, PMimNTf2.

4. Thermodynamic correlation

For the correlation of the experimental data, two excess Gibbs free energy models were applied: the NRTL [13] and UNIQUAC [14] models. The NRTL and UNIQUAC binary interaction parameters of the ternary systems correlated are listed in Table 2 and 3, as well as the values of the root mean square deviation of the composition, σx, and the mean error of the solute distribution ratio, $\Delta\beta$. These deviations were calculated as follows:

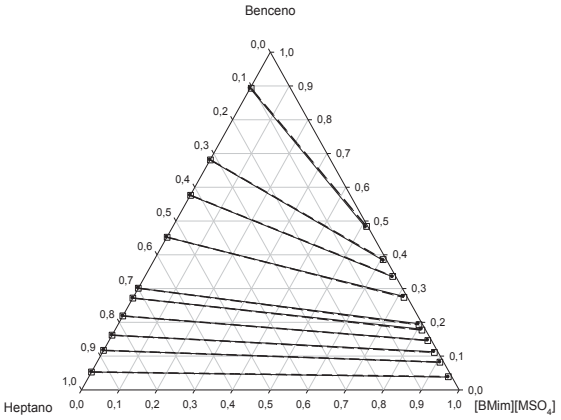
$$\sigma x = 100\sqrt{\frac{\sum_{i}^{M}\sum_{j}^{N-1}\left(\left(x_{ij}^{I,\exp}-x_{ij}^{I,calc}\right)^2+\left(x_{ij}^{II,\exp}-x_{ij}^{II,calc}\right)^2\right)}{2MN}} \tag{3}$$

$$\Delta\beta = 100\sqrt{\frac{1}{M}\sum_{k}\left(\frac{\beta_k-\beta_k^{calc}}{\beta_k}\right)^2} \tag{4}$$

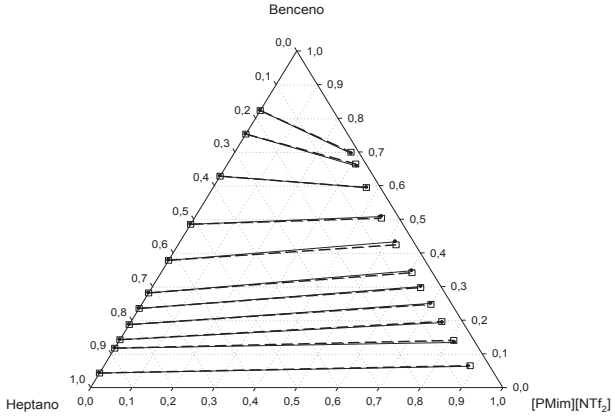
where M is the number of tie-lines and N the number of components in the mixture.

The experimental LLE data are plotted in Figure 2 together with the correlation obtained with the NRTL model. As can be seen in Figure 2, the miscible region decreases when the NTf_2- anion is changed by MSO_4 anion. As can be inferred from Table 2 and 3, both models fit satisfactorily the experimental data, presenting small deviations.

a)



b)



c)

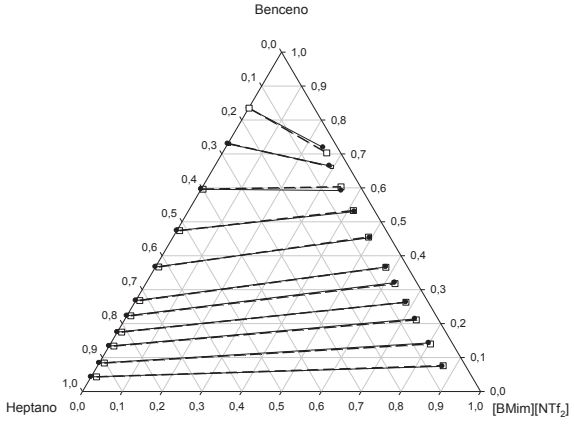


Fig. 2. Experimental LLE of the ternary systems, a) heptane (1) + benzene (2) + $BMimMSO_4$ (3); b) heptane (1) + benzene (2) + $BMimNTF_2$ (3) and c) heptane (1) + benzene (2) + $BMimNTF_2$ (3) solid lines and full points indicate experimental tie-lines and dashed lines and empty squares indicate calculated data from NRTL model.

Table 2. NRTL binary interaction parameters and deviations for LLE data of ternary systems with $\alpha = 0.1$

i-j	Δg_{ij}/(kJ·mol^{-1})	Δg_{ji}/(kJ·mol^{-1})	σx	Δβ
heptane (1) + benzene (2) + BMimMSO4 (3)				
1-2	-10.144	15.912	0.123	3.12
1-3	428.84	10.801		
2-3	39.991	-6.766		
heptane (1) + benzene (2) + BMimNTF2 (3)				
1-2	-9.336	23.368	0.071	2.85
1-3	173.238	11.917		
2-3	31.788	-3.311		
heptane (1) + benzene (2) + PMimNTF2 (3)				
1-2	2.6701	-7.0799	0.223	2.01
1-3	25.656	-1.2262		
2-3	37.112	-16.050		

Table 3. UNIQUAC binary interaction parameters and deviations for LLE data of ternary systems

i-j	Δu_{ij}/(kJ·mol^{-1})	Δuji/(kJ·mol-1)	σx	Δβ
heptane (1) + benzene (2) + BMimMSO4 (3)				
1-2	-0.0671	0.9664	0.550	2.86
1-3	186.70	0.1672		
2-3	1.1891	0.5353		
heptane (1) + benzene (2) + BMimNTF2 (3)				
1-2	0.6412	-0.0142	0.145	1.44
1-3	1.9753	0.3954		
2-3	3.5571	-15997		

To study the influence of the structure of ionic liquids on the separation of aliphatic and aromatic, three ternary LLE including heptane, benzene and three ionic liquids were carried out at 298.15K.

Regarding the influence of the anion, comparing the behavior of the three systems, it can be observed that the *S* values are higher for the system containing $BMimMSO_4$, and on the other hand, the β values are higher where $BMimNTf_2$ is used as solvent, being higher than the unity at lower compositions of benzene

in the upper phase. The influence of the alkyl chain of the cation of the IL is lower than the influence of the anion on the phase equilibrium; and it can be concluded that selectivity values of the systems containing imidazolium-based ILs with NTf_2^- anion are similar, while it can be observed that β values slightly increase in the order $BMimMSO_4$ > $PMimMSO_4$. Experimental data were satisfactorily correlated using the NRTL and UNIQUAC thermodynamic models.

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